

The Structure of Organic Crystals.¹

By SIR WILLIAM BRAGG, K.B.E., F.R.S.

IT may be said with truth that modern advances in physical science are due in the main to the acquisition of the power to handle the individual atom. Until the present time we have always attacked the problems of matter by examining the behaviour of atoms or molecules in groups. The new powers arise in two ways :—

In the first the individual atom is endowed with excessive speed and energy, and is able to make its individuality felt on this account. The α -particle of the radioactive radiations is a helium atom moving with a speed of the order of one-tenth of that of light. While in possession of the relatively tremendous energy which the speed implies it can, unaided, make a visible impression on a fluorescent screen. It can pass through thousands of other atoms without sensible deviation and, if occasionally it suffers violent deflection, it has penetrated to the very core of the atom which has deflected it. Rutherford has shown us what important deductions can be drawn as to the construction of the atom by examining these rare and sharp deviations, and is going even further in examining the shattering effect which the deflecting atom may itself experience. So also, the electron endowed with sufficient speed can traverse matter and bring about its ionisation and other effects of great interest, but if its velocity becomes less than one million metres per second this free existence disappears. It is attached to the first atom it meets.

The second method of attack upon the individual atom proceeds on very different lines. It is by way of the mutual action of X-rays and crystals. When we are examining things by eyesight we follow the influence of the objects that we look at upon the waves of light. If we wish to penetrate deeper into the minute, we take advantage of the optical effects of lenses and build microscopes: but, even then we cannot attack individual objects containing less than many thousands of individual atoms. A limit is set by the difficulty that light cannot show us the form of things which are much smaller than the wave length of the light itself. With the aid of the very short waves known as X-rays we can make our way down to objects ten thousand times smaller, but by itself this extension of our powers would be inefficient, because the effect due to one atom or one unit of pattern would be inappreciable. Here lies the value of the crystal, which, being an aggregate of some small atomic pattern repeated again and again through space, shows up on a measurable scale the properties of the atoms in the single unit. By the combination of X-ray and crystal we can examine the very foundations of material construction. It is difficult to set a limit to what may be the consequences of the exercise of these powers since we can now examine all physical effects, so to speak, at their source, and must in the end be able to refer all the physical and chemical properties of materials to the properties of the individual atoms and their mutual forces. So far the new methods have scarcely begun to show their full strength. A few inorganic crystals have been examined with a view of discovering

their structure, but the new field of research is barely entered. Inviting roads lie before us pointing in numerous directions.

Very little has yet been done in the way of applying the new methods to the structure of organic crystals, although no study could be more tempting. Their vast variety of form, the perfection of their structure, their importance, all urge us forward, and especially the fact that the whole progress of organic chemistry shows that the science depends upon laws of position with which the X-rays are especially qualified to deal. The difficulty at the outset lies in the complexity. In the naphthalene molecule there are 18 atoms: in what way can we expect by means of X-rays to solve the intricate problem of their relative positions? Our first attempts to solve inorganic crystals depended for their success upon two facts :—

The first, the simplicity of the structures which were attacked.

The second, the guidance derived from the principles of crystallographic symmetry.

The determination of the structure of rocksalt opened a way to further determinations of such simple crystals as the diamond, zinc blende, fluorspar, and others. In all these the principles of symmetry supplemented the knowledge derived from the examination of the intensities of X-ray reflection by the various crystal planes. As the work has proceeded in the hands of observers in many countries, other principles have emerged or are emerging which render further and very valuable aid so that problems appear to be coming within our grasp that not long ago seemed most difficult of solution.

Of these principles, one began to appear in consequence of the very earliest results. It was a very striking fact that in crystals of polar substances the molecule seemed to disappear; it was in fact dissociated, and the structure of the crystal depended upon the grouping of the positive ions round the negative and of the negative ions round the positive. In rocksalt each metal atom is surrounded by six atoms of chlorine and *vice versa*. If we accept this as an indication of the general character of such structures, adding to it the condition that every atom is to be like every other atom of its own kind in respect to relative distances and orientations of all its neighbours, it becomes possible to foretell the probable form of structure, using the X-ray methods for subsequent verification. This method of proceeding may be very much easier than if it were taken in the reverse way. We might for example have gone far to foretell the structure of fluorspar. It is an ionic compound in which the calcium atoms are doubly charged and fluorines are singly charged. Each positive is to be surrounded, therefore, by twice as many neighbours as each negative by positive. The fluorspar structure in which the metal atoms are arranged at the corners and the face centres of the cube, while the fluorines lie at the centres of the eight small cubes into which the larger ones can be divided is one of the very few regular ways in which this numerical relation of 2 to 1 can be carried out. So also in ice, the 2 to 1 arrangement is

¹ Discourse delivered at the Royal Institution on Friday, May 19.

carried out in a second of these ways, the relative numbers of neighbours being four to two. It is the lightest and most open of the 2 to 1 structures, and is consistent with the low specific gravity of ice and with the possibility of compressing the substance into denser forms: at the same time it shows the six-pointed arrangement and the featheriness of the snow crystal.²

The earlier results at the same time showed that in the diamond we had a construction of very different properties and nature. Here the atoms are electrically neutral and are bound to one another, not by electrical attraction from centre to centre, but by a more intimate process which probably consists in some way of a sharing of structural electrons. The diamond is on this account the hardest of known substances.

These considerations amount to a recognition that the bonds between the atoms may be of very different characters though it may be difficult to draw hard and fast lines between them. We can say that there is a very strong electron sharing bond of which the diamond is typical, and that there are ionic bonds in polar compounds which in general are of a weaker character, as, for example, in rocksalt, though on the other hand they may be strong when, as in the ruby, the ionic charges are large.

Lastly, there is a third type, which is found in the organic crystal, where it would appear that the separate molecule can be distinguished. The atoms in each molecule are strongly tied together, but the forces that bind molecule to molecule may be described as residual. They would appear to be weak fields concentrated at definite points on the molecule, the positive and negative charges to which they are due lying within it.

The second principle which emerged fairly early in the experiments was described by my son in an address which he gave in this Institution some time ago.³ We may call it the principle of radii of combination. The distance between the centre of one atom and the centre of a neighbour can in many cases be measured with great accuracy: we can compare these distances when substitutions are made in isomorphous compounds. The replacement of fluorine by chlorine, chlorine by bromine, bromine by iodine in a series of salts produces changes in the distances which imply that the radius of any one of the atoms mentioned may be treated as a constant within the range of the substitution considered. The accuracy is amply sufficient to give useful assistance in crystal analysis. It would not be true, however, to say that each atom has an invariable radius, and indeed the original statement of the principle purposely refrained from going so far. It is not right to speak of the *radius* of an atom; it is better to speak of a *radius of combination*. We may take an illustration from the behaviour of arsenic, antimony, and bismuth. The crystals of these substances are trigonal in form,⁴ plainly showing that the properties of each atom are not the same in all directions within the crystal: in fact, analysis shows that each atom is fastened to three on one side of it by much closer bonds than to three atoms on the other side. One bonding resembles more closely that of the diamond, the other

that of a metal where free electrons keep the atoms together by electrostatic attraction. It may be said that the atom behaves as a metal on one side and a non-metal on the other. At any rate, there are two radii of combination varying with the nature of the bond. The metallic bond is the weak one and the cleavage plane cuts only through such bonds. It seems very likely that in this way we can understand the formation of crystals of different type when these elements enter into their composition. For example, in the cubic form of senarmontite (Sb_2O_3) the atoms of antimony are completely separated; each touches six atoms of oxygen, while each oxygen touches four atoms of antimony. Antimony is here behaving as a metal only, so that we represent it in a model as a sphere, and the uniform spheres of antimony and of oxygen naturally build into a simple crystal. It is a cube in which the atoms of antimony occupy the corners and centres of the faces while the six oxygen atoms lie at the centres of six of the eight small cubes into which the large one can be divided.

There is, however, an alternative form of Sb_2O_3 known as valentinite, which is ortho-rhombic. Analysis, so far as it has gone, though it is not yet complete, points emphatically to the conclusion that here atoms of antimony are pairing, the bonds between the members of a pair being of the stronger variety already referred to. We now have an elementary body of a dumb-bell shape which, when forming part of the crystal structure, will naturally cause a deviation from a simple cube.

Yet again, there are principles which are barely established as yet, though it seems probable that they will be found of material assistance in analysis. The greater expansion of some crystals in certain directions than in others seems to depend upon the nature of the bonds. Bismuth expands more along the axis than across it, as we might expect from the fact that in the one expansion the weak bonds alone can be operative. In the same way diamond has an extremely small expansion co-efficient because all the bonds are of the strongest kind, but in graphite, on the other hand, the expansion along the axis may be described as enormous. Mr. Backhurst finds an increase in length of 3 per cent. for a rise of 900°C . At the same time, so far as can be inferred, the expansion across the axis is still quite small. In one case weak bonds only are concerned, in the other, strong bonds of the same kind as in the diamond.

It is when all these considerations are taken into account that it seems possible to make an attempt upon the structure of the organic crystals. They are, of course, very complex; naphthalene contains 10 atoms of carbon and 8 atoms of hydrogen, and our ability to interpret X-ray evidence, that is to say, the relative intensities of reflection by the different planes in different orders, is not sufficiently advanced to enable us to place so many atoms in their proper position in the cell from this evidence alone. We can readily find the size of the unit cell, show that there are two molecules in it, and that the points, each of which represents a whole molecule, are to be placed as is shown in Fig. 1, but without some further help we can frame no hypothesis on which to proceed.

Suppose now that we compare the structures of diamond and graphite. As my son showed long ago,

² Proc. Phys. Soc., London, vol. xxxiv, pt. 3, p. 98.

³ See *Phil. Mag.*, Aug. 1920.

⁴ James and Tunstall, *Phil. Mag.*, Aug. 1920 and July 1921; Ogg, *Phil. Mag.*, July 1921.

the structure of graphite must be derivable from that of the diamond by separating to nearly double their previous distance the sheets of atoms parallel to one of the cleavage planes of the latter crystal. The question has been very carefully considered more recently by Hull in America and by Debye and Scherrer on the Continent in the hope of finding more exactly the details of the movement: they do not quite agree.

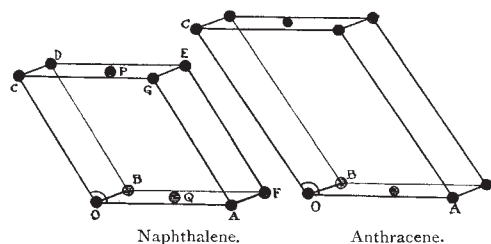


FIG. 1.—Unit cells of naphthalene and anthracene drawn to the same scale.

	OA = a.	OB = b.	OC = c.
Naphthalene	8.34	6.05	8.69
Anthracene	8.7	6.1	11.6
Naphthalene	$\alpha = \text{BOC} = 90^\circ$, $\beta = \text{COA} = 122^\circ 49'$, $\gamma = \text{AOB} = 90^\circ$		
Anthracene	$\alpha = \text{BOC} = 90^\circ$, $\beta = \text{COA} = 124^\circ 24'$, $\gamma = \text{AOB} = 90^\circ$		

Fig. 2 represents the change as described by Hull. The bonds between the atoms in each sheet are unaffected apparently, but those between sheet and sheet are replaced by something much weaker. The diamond is typical of hardness, the graphite is used as a lubricant. If the hexagonal rings of which the sheets are formed have survived this violent change, why not suppose that they may survive the further change when the sheets break up into ring structures? In other words, suppose that the benzene ring is really a fact, not merely a diagram; the distance between atom and atom in

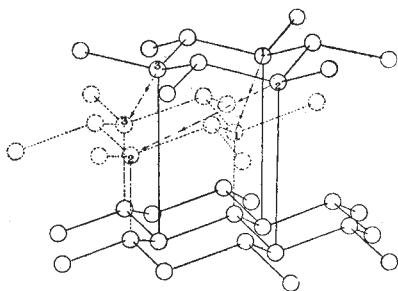


FIG. 2.—The fine lines of the diagram show the structure of graphite. By moving the top layer to the position shown by the broken lines the diamond structure is obtained.

the ring is $1.54 \text{ \AA.U.}$ as in the diamond, and perhaps we may add that the atoms are not all in one plane, but are arranged, as may be seen in Fig. 3. We then proceed to test this hypothesis by finding whether we can fit together molecules of the assumed size and shape into the cells which hold them. From X-ray studies we know the exact form and dimensions of the cells, and can learn also much concerning the relative distributions of the molecules within them. It appears at once that in the few simple cases which have been examined an excellent fit is possible and, more than that, we find encouraging signs that the structural idea has been chosen rightly. For instance, the comparison of the cells of naphthalene and anthracene, one a two-ring, the other a three-ring combination,

shows that two of the axes of the cell remain constant, while the third has grown by an amount which is nearly the width of the benzene ring. From these and various other indications we build a structure such as is represented in Figs. 3 and 4. It would seem that the molecules are linked together side to side more strongly than from end to end, and that is why these and similar crystals cleave across the end or β position.

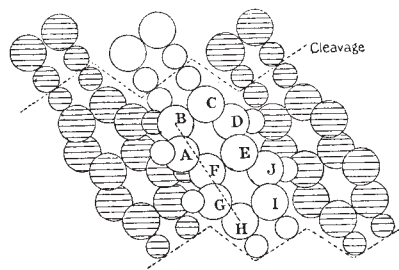


FIG. 3.—Showing mutual relations of three naphthalene molecules and parts of others.

The unshaded circles between the two cleavage planes represent a molecule as at Q (Fig. 1). The shaded represent molecules B and F in the same figure. The small circles represent hydrogen atoms, but their size is uncertain.

Diameter of carbon atom = 1.50 . $BH = 4.92$. Projection of AD on the plane of the diagram = 2.50 . Benzene ring consists of atoms A...F only.

If we examine α -naphthol in which hydrogen at the side of the naphthalene molecule has been replaced by an OH group, we find that the standard cell contains four molecules, which is what we should expect, for each of the four α positions must be represented. When the OH group is taken from the side and put at the end, we find that the cell has shrunk sideways and grown lengthways by the amount we should expect to result from the addition of an oxygen atom. When as in acenaphthene a complex group of atoms is attached to one side of the molecule and the crystal

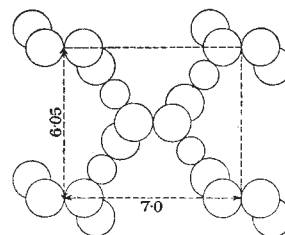


FIG. 4.—Section of naphthalene cell perpendicular to the axis of c, showing α -hydrogens connecting the molecules side to side.

to our surprise becomes more regular than before, right angled instead of oblique, we find an explanation in the fact that there are now four molecules within the cell instead of two, and that by sloping in pairs in opposite ways they increase the symmetry of the crystal.

These examples may serve to show how an attempt may be made to arrive at a knowledge of the structure of these organic compounds with, I think, some success. It seems justifiable to see in the rigid and queerly shaped molecule attaching itself at definite points, and with great precision of orientation to neighbouring molecules, a cause of the immense multiplicity and, at the same time, the accurate form of organic crystals, and indeed to find here the foundations of organic chemistry.